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Reaction kinetics and oxidation product formation in the degradation of acetaminophen by ferrate (VI)

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Abstract

This paper investigates the degradation of acetaminophen (AAP) in aqueous solutions by ferrate (VI), aiming to propose the kinetics, pathways and the oxidation products' formation in the AAP degradation. A series of jar tests were undertaken over ferrate (VI) dosages (molar ratios of ferrate (VI):AAP, 5:1 to 25:1) and pH values (4~11). The effects of co-existing ions (0.2~5 mM) and humic acid (10~50 $mg \cdot l^{-1}$) on the AAP removal were investigated. Ferrate (VI) can remove 99.6 % AAP (from 1000 $\mu g \cdot l^{-1}$) in 60 minutes under study conditions when majority of the AAP reduction occurred in the first 5 minutes. The treatment performance depended on the ferrate(VI) dosage, pH and the type and strength of co-existing ions and humic acid. Raising ferrate (VI) dosage with optimal pH 7 improved the AAP degradation. In the presence of humic acid, the AAP degradation by ferrate (VI) was promoted in a short period (< 30 min) but then inhibited with increasing in humic acid contents. The presence of Al^{3+}, CO_3^{2-} and PO_4^{3-} ions declined but the existence of K^+, Na^+, Mg^{2+} and Ca^{2+} ions can improve the AAP removal. The catalytic function of Al^{3+} on the decomposition of ferrate (VI) in aqueous solution was found.

The kinetics of the reaction between ferrate (VI) and AAP was pseudo first-order for ferrete (VI) and pseudo second-order for AAP. The pseudo rate constant of ferrate (VI) with AAP was 1.4×10^{-5} $L^2 \cdot mg^{-2} \cdot min^{-1}$. Three oxidation products (OPs) were identified and the AAP degradation pathways were proposed.

Keywords: Potassium ferrate (VI); Acetaminophen; Reaction mechanism; Influence factors; Oxidation products

1. Introduction

In recent years, pharmaceutical and personal care products (PPCPs) have been detected in numerous water resources (Boyd et al., 2003; Kim et al., 2009; Liu and Wong, 2013). The potential hazard toward aquatic organisms and public health (Fent et al., 2006; Crane et al., 2006; Witorsch and Thomas, 2010) resulting from increasing PPCPs concentrations, and the incomplete removal of PPCPs has been found in various conventional wastewater treatment plants (Boyd et al., 2003; Khetan and Collins, 2007). As a typical anti-inflammatory and analgesic medication, acetaminophen (AAP) is produced and consumed about 1.45×10^5 tons per year worldwide (Kasprzyk-Horderna et al., 2008). AAP has high solubility up to 12.78 $g\cdot kg^{-1}$ in aqueous solutions at 20 °C, and has been detected frequently in water courses (Granberg and Rasmuson, 1999). More than 65 μg/L of acetaminophen has been detected in surface water and the concentration of acetaminophen might be much higher in pharmaceutical industry wastewater (Roberts and Thomas, 2006). Research has shown that AAP had toxicity on bivalve *Dreissena polymorpha* (Parolini et al., 2013).

Due to the possession of dual functions of oxidation and coagulation, ferrate (VI) has been studied widely and demonstrated to be a very promising chemical for both water and waste water treatment (Jiang and Lloyd, 2002; Lee et al., 2004; Jiang et al., 2006). The elimination of PPCPs by ferrate (VI) has been conducted by many researchers (e.g., Yang et al., 2012; Jiang et al., 2013; Jiang, 2014; Sharma et al., 2015). So far, the degradation of AAP has been reported by anodic oxidation with a

boron-doped diamond electrode (Brillas et al., 2005), subsurface flow constructed wetlands (Ranieri et al., 2011), ozonation and H_2O_2/UV system (Andreozzi et al., 2003), Photo-Fenton process (Trovo et al., 2008) and TiO_2 photocatalysis (Yang et al., 2008). However, to the best of our knowledge, the study on the degradation of AAP using ferrate (VI) has not been reported so far.

And thus, this study focused on the removal of AAP in aqueous solutions by ferrate (VI). Conditions of the degradation of AAP were investigated with respect to ferrate (VI) dosage, pH value, and the presence of humic acid and various co-existing ions (K^+, Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}). The study also aimed to reveal oxidation products (OPs) and kinetics for the degradation of AAP by ferrate (VI).

2. Experimental section

2.1 Chemicals and reagents

Acetaminophen (AAP) was purchased from aladdin (Shanghai, China); Sodium hydroxide, methanol (LC) and potassium hydroxide (AR) were purchased from Hangzhou Xiaoshan Chemical Reagent Factory (Hangzhou, China); Humic acid (HA) was obtained from Nanjing Chemical Reagent Factory (Nanjing, China). Ferrate (VI) solution of high concentration was synthesized by the electro-chemical way (Wang et al., 2015), and then transferred to solid potassium ferrate (VI) after various purification steps (Li et al., 2005). The ferrate(VI) strength of the resulting dry product was measured by chromite method and direct spectrophotometric method

using a wavelength of 505 nm and an absorbance coefficient of 1100 $M^{-1} \cdot cm^{-1}$ (Jiang et al., 2009). The purity of ferrate (VI) was continuously monitored on the daily basis. The other reagents were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Experimental water was generated by ultra pure water supplier (UPHW1-90T, Sichuan europtronic ultra pure Technology Co. Ltd., China). Stock solutions of AAP were prepared in pure water at 100 $mg \cdot l^{-1}$ for the use of jar test experiments, identification of oxidation products and kinetic analysis.

2.2 Jar test experiment

The oxidation of AAP by ferrate (VI) was studied using a magnetic stirrer (Color squid, IKA (Guangzhou) equipment Co. Ltd, China) with a mixing speed of 600 rpm. Pipette (Shanghai Kangmin inspection equipment Co. Ltd, China) was used for sampling at given reaction time intervals; 1, 2, 5, 10, 20, 40 and 60 min, respectively, and sodium hyposulfite was used as a quencher.

In order to examine the formation of AAP oxidation product as well as to assess the degradation performance readily, two initial AAP concentrations, 500 and 1000 $\mu g \cdot l^{-1}$ respectively, were used for the study. The selected AAP concentrations were also in line with that used by other researchers (e.g., Yang et al., 2008). The influence of operating conditions were investigated using 100 mL test solutions with initial AAP concentrations of 1000 $\mu g \cdot l^{-1}$ and by adjusting a number of ferrate (VI) dosages, pH values and HA concentrations. Ferrate (VI) was dosed into the test solution as dried powder and the dosage applied was in the molar ratio of ferrate (VI):AAP from 5:1 to 25:1. The pH of test solutions was adjusted by 0.01 M hydrochloric acid and 0.01 M

sodium hydroxide to pH 4~11. The HA concentration in testing solutions was 10~50 $mg \cdot l^{-1}$.

Test solutions of 200 mL with AAP initial concentration of 500 $\mu g \cdot l^{-1}$ were used to study the impact of the presence of 0.2~5 mM co-existing ions (K^+, Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, CO_3^{2-}, SO_4^{2-},PO_4^{3-}) on the AAP degradation performance by ferrate(VI). The AAP solutions were mixed with given amount of NaCl, KCl, $MgCl_2$, $CaCl_2$, $Al_2(SO_4)_3$, Na_2CO_3, Na_2SO_4 and Na_3PO_4, respectively, to achieve the required ion concentrations. The ferrate (VI) with dosage of the molar ratio of 28:1(ferrate (VI):AAP) was mixed with the test solution and the sampling time was 0, 1, 2, 3, 5, 7 and 15 min. All samples in jar test experiments were filtered by 0.45 μm glass membrane filters (Shanghai Xingya purifying material factory, China) before analyzing the residual AAP concentrations. The AAP concentration and removal percentage of each sample were detected by liquid chromatography (LC) (see sub-section 2.5).

2.3 Identification of degradation products

Test solutions of 1000 $\mu g \cdot l^{-1}$ AAP were prepared in pure water. Ferrate (VI) was added to the solution of AAP with the molar ratio of 40:1. The samples were obtained after determined intervals, 0, 1, 5, 15, 30, 45 and 60 min. Detailed procedures of identification of AAP degradation products can be seen in sub-section 2.5.

2.4 Kinetic analysis

Kinetic analysis of AAP with ferrate (VI) was performed at room temperature

131 (20±2^{0}C) under pseudo-first-order conditions with ferrate (VI) in excess. The test
132 solutions of AAP were prepared in pure water. A given ferrate (VI) dose of 32.5 mg·l$^-$
133 ^{1} was added into test solutions with AAP concentrations of 300, 500, 700, 900 μg·l^{-1}
134 respectively. On the other hand, several ferrate (VI) doses, 13, 19.5, 26, 32.5 mg·l^{-1}
135 respectively, were dosed into the test solutions with a given AAP concentration of
136 1000 μg·l^{-1}. For the given time intervals as stated above, the reacting solutions were
137 quenched with sodium hyposulfite solution.

138 *2.5 Analytical methods*

139 The concentration of chemical oxygen demand (COD) of test solutions before
140 and after ferrate (VI) treatment was measured by potassium dichromate method
141 (APHA et al., 1998).

142 Ion chromatograph (ICS-900, Dionex, US), coupled with an anion column
143 (IonPac AS19, 4×250 mm) and a flow rate of 0.8 mL·min^{-1} of 20 mM KOH solution,
144 was used for the measurement of inorganic ions' concentrations.

145 The measurement of AAP was conducted by an Agilent 1200 LC system
146 (Agilent, US) with diode array detector (DAD). The column utilised for the separation
147 of compounds was a 5 μm, 4.6×150 mm reversed phase Eclipse XDB-C18 column
148 (Agilent, US). The column was kept at 30 ^{0}C and eluted by 15% methanol and 85%
149 pure water at a flow rate of 0.8 mL·min^{-1}. The injection volume was 10 μl and the
150 DAD detection wavelength for AAP was 257 nm.

151 The oxidation products of AAP treated by ferrate (VI) were analyzed by a GC-
152 MS system (Saturn, USA) equipped with an SE-54 capillary column (Chromse, UK).

153 For each GC-MS injection, samples were pretreated by hydrochloric acid of 1 M to
154 pH<1 and then extracted with chloroform (10 times concentrated). The GC conditions
155 were given as follows: a sample volume of 1 μl injected in the splitless mode at 280
156 ^{0}C and the oven temperature programmed from 50 ^{0}C (5 min) to 250 ^{0}C at 10 ^{0}C min^{-1}
157 followed by a 5 min hold at 250 ^{0}C, and helium used as the carrier gas at a flow rate
158 of 0.8 ml min^{-1}. Mass spectrometer was operated under electron ionization mode at 70
159 eV with mass scan range of 40~500.
160
161 **3. Results and discussion**
162 *3.1. Effect of reaction time and ferrate (VI) dosage*
163
164 Fig. 1. Effect of reaction time and ferrate (VI) dosage on AAP degradation
165 Fig.1 shows the variation of AAP degradation efficiency vs. reaction time and
166 ferrate (VI) dosages. The removal of AAP by ferrate (VI) mainly occurred within the
167 first 5 min reactions, followed by a more gradual further removal over the next 10～
168 55 min. Increasing in the ferrate (VI) dose (as molar ratio of ferrate (VI): AAP) from
169 5:1 to 25:1, the removal efficiency of AAP increased sharply for the given time of 60
170 min; that the AAP removal percentage was 50.5, 76.7, 96.9 and 99.6% for the molar
171 ratio of 5:1, 10:1, 15:1 and 25:1, respectively. On the other hand, for a 10 min
172 reaction and high ferrate(VI) dose (molar ratio of 25:1), approximate 90% AAP was
173 removed. In general, ferrate (VI) could remove AAP readily under these conditions.

Additionally, COD concentration of the test solution with 10 mg AAP l^{-1} was 31 mg l^{-1} and after ferrate(VI) treatment (ferrate (VI) dose of 0.325 g/L) the COD was reduced to 24 mg l^{-1} which gives 23% COD reduction, representing the optimal COD reduction performance.

3.2. Effect of pH

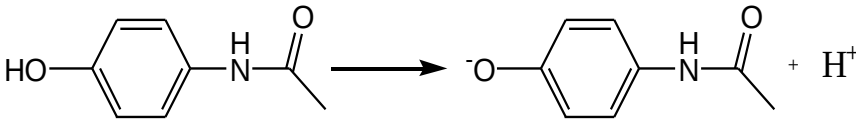
Fig.2 shows the variation of AAP degradation efficiency vs. pH value and reaction time. It can be observed that for a given ferrate(VI) dose (25:1 as molar ratio, ferrate (VI):AAP) and pH 4, AAP removal was about 85% and irrelevant to the reaction time. For other pHs, AAP removal was less than 70% and pH 11 was not favorable to the APP removal especially for short reaction time; only 11.3% AAP was removed for the reaction time of 2 min at pH 11. On the other hand, increasing in reaction time was favorable to the AAP removal for pH 6-9; 60 min reaction gave the greatest AAP removal (99.95%) for pH 7. Moreover for pH 4 and 9, the degradation rate of AAP by ferrate (VI) increased rapidly at the initial reaction period (2 min) but approached to slight variations after 10 min.

Fig. 2. Effect of different pH values on AAP degradation

pH of test solution affects on the oxidation capacity and stability of ferrate (VI). As shown in Fig. 2, degradation rate of AAP by ferrate(VI) at pH 4 was superior to

195 that at pH 11, since ferrate (VI) possesses higher redox potential (2.2 ev) under acidic
196 conditions than that for alkaline conditions. Moreover, ferrate (VI) has been reported
197 to be dissociated to form different species in terms of solution pH as shown in
198 equations 1-3 (Sharma, 2002) and in Fig. S1 of the supplementary material.
199
200 $H_3FeO_4^+ \longleftrightarrow H^+ + H_2FeO_4, PK_a = 1.6 \pm 0.2$ (1)
201 $H_2FeO_4 \longleftrightarrow H^+ + HFeO_4^-, \quad PK_a = 3.5$ (2)
202 $HFeO_4^- \longleftrightarrow H^+ + FeO_4^{2-}, PK_a = 7.3 \pm 0.1$ (3)
203
204 For pH 4 or less, major ferrate (VI) species are $H_3FeO_4^+$, H_2FeO_4 and $HFeO_4^-$,
205 which are readily self-decomposed, resulting in rapid oxidation of APP which has
206 been demonstrated in Fig. 2 where the AAP removal was about 85% and irrelevant to
207 the reaction time. Relatively for pH 7, ferrate (VI) was stable and still had high
208 oxidizing ability and then the best AAP removal performance was achieved for a long
209 reaction duration (60 min).
210 The second effect of pH on the AAP degradation is attributed to the dissociating
211 products of AAP. The PK_a of AAP was 9.5, and dissociating and/or protonated species
212 could be dominant when pH was 9 (see equation 4). Fig. 2 shows that for pH 9, the
213 AAP removal efficiency was high and it was close to that at pH 7. Hence, the results
214 observed from this study demonstrated that high protonated AAP species were readily
215 degraded by ferrate (VI), which is consistent with that from the reported work where
216 solutions containing phenol and chlorinated phenols were treated by ozone and ferrate

(VI) (e.g., Graham et al., 2004).



(4)

3.3. Kinetics

The rate expression for the reaction of ferrate (VI) with AAP can be expressed as

$$r = -d[AAP] \cdot d_T^{-1} = -k \cdot [Ferrate(VI)]^a \cdot [AAP]^b \quad (5)$$

where *r* represents the reaction rate of ferrate (VI) with AAP, *k* represents the overall rate constant of ferrate (VI) with AAP, *a* and *b* represent the orders of the reaction, [Ferrate(VI)] and [AAP] represent the concentrations of ferrate (VI) and AAP. The kinetic studies were carried out under pseudo-order conditions with ferrate (VI) in excess. Eq. (5) can be rewritten as

$$r = k_1 \cdot [AAP]^b \quad (6)$$

Where

$$k_1 = k \cdot [Ferrate(VI)]^a \quad (7)$$

Eq. (6) can be rewritten as

$$\ln r = \ln k_1 + b \ln[AAP] \quad (8)$$

Eq. (7) can be rewritten as

$$\ln k_1 = \ln k + a \ln[Ferrate(VI)] \quad (9)$$

Table1. Kinetic parameters of AAP degradation by ferrate (VI)

Table 1 shows the initial concentrations of AAP, ferrate (VI) dosage, fitting equations and initial reaction rate of AAP. It can be seen that the plot of the reciprocal of AAP concentrations versus reaction time were linear with good coefficient of correlation (R^2>0.90) at various concentrations of ferrate (VI), indicating the reaction was second-order with respect to ferrate (VI). Moreover, the plot of the natural logarithm of AAP concentrations versus reaction time were linear with good correlation coefficient (R^2>0.90) at various concentrations of AAP, indicating the reaction was first-order with respect to AAP. Although ferrate (VI) was unstable, ferrate (VI) was always in excess in comparison to AAP within the studied reaction time. The value *a* could be obtained as the slope of ln r versus ln[AAP] with linear fitting and the *b* is to be determined as the slope of ln k_1 versus ln[Ferrat(VI)] with linear fitting, and this can be seen in Figure 3. Thus, the values of *a* and *b* are 1.2 (R^2=0.999) and 0.38 (R^2=0.939), respectively. The apparent third-order rate constant (k) for the reaction was calculated through the intercept in vertical axis. The value of k is 0.000014 $L^2 \cdot mg^{-2} \cdot min^{-1}$. The observed rate law can be written in terms of both ferrate (VI) and AAP as

$$r = -d[AAP]d_T^{-1} = -0.000014 \cdot [Ferrate(VI)]^{1.20} \cdot [AAP]^{0.38} \quad (10)$$

Fig. 3. Kinetic analysis of AAP degradation by ferrate (VI)

3.4. Oxidation products

Based on the measured m/z values and prior literature (Andreozzi et al., 2003; Yang et al., 2009; Moctezuma et al., 2012), the best-fit chemical structures of oxidation products (OPs) were tentatively proposed by considering the molecule pattern of target compounds and the mechanism of ferrate (VI) oxidation; and the probable structures of OPs (AAP-1-3)are presented in Fig. 4. AAP would be attacked by ferrate (VI) which leads to the cleavage of imino group and the transformation of acetyl amino group, forming AAP-1 and AAP-2 respectively. The formation of AAP-3 might attribute to further oxidation of intermediate OPs by ferrate (VI). Besides, the NO_3^- was detected in the reaction solution which is consistent with previous studies (Skoumal et al., 2006; Yang et al., 2009), and suggests that the possibility of the broken of C-N bonds.

Fig. 4. Detection of oxidation products (a – c) and original compound, AAP (d)

Fig. 5. Evolution of OPs and nitrate with decreasing of AAP concentration

Fig.5 shows the evolution of OPs and nitrate during the AAP degradation by ferrate (VI). As it can be observed, AAP-1-2 were formed from the first 1 min reaction, but almost disappeared, together with the AAP, after 60 min reactions. AAP-3 was detected after 15 min and trace nitrate (C_{max}=0.038 mg l^{-1}) was detected in the degradation process. These results also indicate that further oxidation of intermediate OPs by ferrate(VI) occurred.

Fig. 6 shows probable pathways of AAP degradation during the treatment by

282 ferrate (VI). The oxidation product, AAP-1, was formed with loss of a C_2H_4NO group
283 from the benzene ring, and the pathway was different with the formation of
284 hydroquinone (Skoumal et al., 2006; Tao et al., 2015) in other AAP degradation.
285 AAP-2 was generated by replacing the hydroxyl group with a quinonyl group and the
286 further loss of a C_2H_3O group from the imino group. In accordance with previous
287 literature (Skoumal et al., 2006; Yang et al., 2008; Moctezuma et al., 2012), AAP-3
288 was also detected, which was a further oxidation product from AAP-1 (phenol).
289 Reference to the prior knowledge (Santos, et al., 2002; Andreozzi et al., 2003; Wang
290 et al., 2014), phenol would be oxidized into para-benzoquinone, which was then
291 converted into maleic acid (AAP-3). The further degradation of AAP-3 could produce
292 oxalic acid and formic acid (Santos, et al., 2002; Skoumal, et al., 2006). Besides, the
293 formation of NO_3^- is due to the deamination of AAP and AAP-2. The attack by
294 ferrate(VI) on the hydroxyl and acetamido groups is consistent with the conclusions
295 made by Zhou and Jiang (2015), that electron-rich moieties were prone to react with
296 ferrate (VI).
297 Fig. 6. Possible pathways of AAP degradation by ferrate (VI)
298

299 *3.5. The presence of humic acid*

300

301 Fig. 7. Effect of different HA dosage on AAP degradation
302

303 The influence of the strength of humic acid (HA) on the removal of AAP by
304 ferrate (VI) treatment was investigated. Fig. 7 shows the changes in residual
305 concentrations of AAP corresponding to HA doses and for the reaction time. As it can
306 be observed, the removal of AAP increased during the intervals between 2 and 10 min
307 after the addition of HA in AAP solutions. However, for 30 and 60 min, the removal
308 efficiency of AAP with HA was less than that of AAP without HA. This suggests that
309 the presence of HA could accelerate the reaction rate of ferrate (VI) and AAP. The
310 observed phenomena might be related to that in the presence of HA, ferrate (VI) could
311 be dissociated to form ferrate (IV) and ferrate (V) which have even greater oxidation
312 capacity (Sharma, 2010) and then assists to the removal of AAP. With increasing in
313 the strength of HA, the removal efficiency of AAP first increased and then decreased,
314 and finally tended to be constant. The high contents of HA could consume more
315 ferrate (VI) in a long reaction time and this might cause the reduction of the removal
316 of PAA for the reaction time of 30 and 60 min.
317
318 *3.6. Effect of coexisting ions*
319 K^+, Na^+, Mg^{2+}, Ca^{2+}, CO_3^{2-}, SO_4^{2-} and PO_4^{3-} ions are common ions in natural
320 water. Aluminum based coagulant is also widely used in water treatment. The effects
321 of above five cations and three anions on the removal percentage of AAP were
322 studied. In the presence of K^+, Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-} ions, the
323 AAP removal efficiencies vs. reaction time are shown in Fig. 8(a) for the ion
324 concentrations of 0.2 mM, in Fig. 8(c) for 1 mM and Fig. 8(e) for 5 mM, respectively.

As it can be seen, K^+, Na^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} ions can enhance the AAP removal, however, Al^{3+}, CO_3^{2-} and PO_4^{3-} ions had the opposite effect. The higher the concentration of Mg^{2+}, the greater the removal rate of AAP. The performance of K^+, Na^+, Ca^{2+} and SO_4^{2-} mainly remained constant with the increasing concentration from 0.2 to 5 mM.

Table 2. Kinetic parameters of the AAP degradation in the presence of eight co-existing ions

Fig. 8(b), Fig. 8(d) and Fig. 8(f) show the linear fitting curve of the reciprocal of ferrate (VI) concentration and reaction time in the presence of the above ions. Table 2 shows the pseudo reaction rate constant (K_{obs}) and correlation coefficient of the linear fitting curves for Fig. 8(b), Fig. 8(d) and Fig. 8(f). The good correlation coefficients (R^2>0.90, except Al^{3+}) indicate that the reactions were pseudo second-order with respect to ferrate (VI), which is consistent with that shown in the previous section. When raising the ions' concentration from 0.2 to 5 mM, the K_{obs} of CO_3^{2-} and PO_4^{3-} ions decreased, from 4×10^{-4} to 6.8×10^{-5} min^{-1} and 5×10^{-4} to 2.2×10^{-5} min^{-1}, respectively, but the K_{obs} of Mg^{2+} increased, from 3.8×10^{-3} to 8.4×10^{-3} min^{-1}. The resulting rate constants are theoretically evident to the observed effect of co-existing ions on the AAP removal by ferrate(VI); that CO_3^{2-} and PO_4^{3-} ions inhabited while Mg^{2+} ions were beneficial to the reaction between AAP and ferrate(VI).

In the presence of metal cations, deprotonation of acid-base functional groups in AAP molecules can be accelerated due to the metal-AAP binding and this might also

348 reduce the AAP pK_a value (Jeffrey et al., 2006). In this work, the addition of K^+, Na^+,
349 Mg^{2+}, Ca^{2+} could enhance the deprotonation of AAP and then to accelerate the
350 removal rate. Besides, hydrogen ion could be generated through the hydrolysis
351 reaction of magnesium ion in aqueous solution. The accumulation of hydrogen ions
352 helped the increase of oxidation potential of ferrate (VI) (Jiang, 2014). It may be the
353 reason that the addition of Mg^{2+} has a greater removal rate of AAP than Ca^{2+}.
354 In the presence of Al^{3+}, CO_3^{2-} and PO_4^{3-} ions and when the concentration of each
355 ion increased from 0.2 to 5 mM, the removal of AAP decreased from 66.7 to 22.4%
356 for Al^{3+}, 74.2 to 36.5% for CO_3^{2-}, and 79.9 to 13.1% for PO_4^{3-}, respectively. The
357 hydrolysis of CO_3^{2-} and PO_4^{3-} in the aqueous solution could raise the alkalinity and
358 then decreases the oxidation potential of ferrate (VI) and causes the reduction of AAP
359 removal efficiency. This phenomenon was even clearly to observe when
360 concentrations of phosphate and carbonate ions were greater.
361
362 Table 3. Effect of aluminum ions on ferrate (VI) concentration
363
364 In this work, the decomposition of ferrate (VI) caused by aluminium ions was
365 found (Table 3). As can be seen when 500 μl of aluminium ions solution was added,
366 the ferrate (VI) concentration decreased by 79%. This might be related to the
367 hydrolysis of Al^{3+} to produce hydrogen ions into solution, (Eq. 11), which then
368 accelerates the decomposition of ferrate (VI) and could lower the AAP removal
369 efficiency.

370 $$Al^{3+} + 3H_2O = Al(OH)_3 + 3H^+ \quad (11)$$

371

372 Fig. 8. Effect of different ions on AAP degradation

373

374 **4. Conclusions**

375 The treatment of AAP in aqueous solutions by ferrate (VI) was investigated.
376 Results demonstrated that AAP can be removed effectively under the experimental
377 conditions. More ferrate (VI) dosage and a neutral solution environment could bring a
378 better performance on the AAP degradation. Besides, the pseudo rate constant of
379 ferrate (VI) with AAP is 0.000014 $l^2 \cdot mg^{-2} \cdot min^{-1}$. Three oxidation products (OPs) were
380 identified. The attack on hydroxyl and acetamido groups of the AAP by ferrate (VI)
381 was proposed to be the main pathway of the AAP degradation scheme. Moreover, in
382 the presence of HA, a short time interval (< 30 min) would favour to but longer
383 reaction time (30-60 min) decreased the degradation of AAP. The presence of K^+,
384 Na^+, Mg^{2+} and Ca^{2+} ions in aqueous solutions can improve the AAP removal
385 efficiency by ferrate(VI), and the most promoting effect of Mg^{2+} was observed. The
386 presence of Al^{3+}, CO_3^{2-} and PO_4^{3-} would decline the AAP degradation performance
387 significantly. The catalytic function of Al^{3+} to the ferrate (VI) decomposition in
388 aqueous solution was found in this work, which explains the negative effect of Al^{3+} on
389 the AAP reduction by ferrate (VI).

390

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Supplementary material

Supplementary material associated with this article can be found in the online version.

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Figure captions

Fig. 1. Effect of reaction time and ferrate (VI) dosage on AAP degradation

Fig. 2. Effect of different pH values on AAP degradation

Fig. 3. Kinetics analysis of AAP degradation by ferrate (VI)

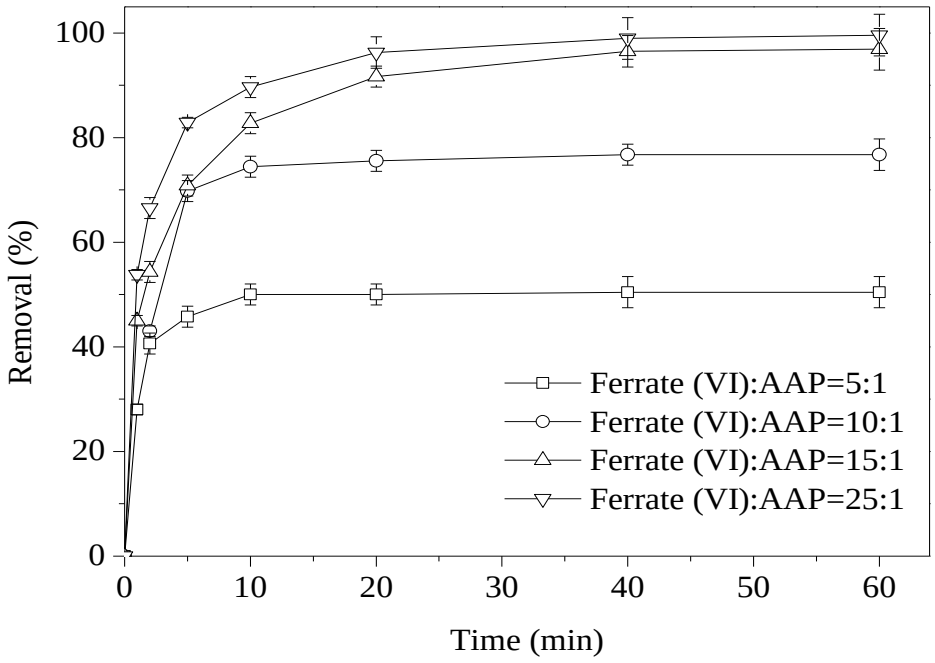
Fig. 4. Detection of oxidation products (a – c) and original compound, AAP (d)

Fig. 5. Evolution of OPs and nitrate with decreasing of AAP concentration

Fig. 6. Possible pathways of AAP degradation by ferrate (VI)

Fig. 7. Effect of different HA dosage on AAP degradation

Fig. 8. Effect of different ions on AAP degradation



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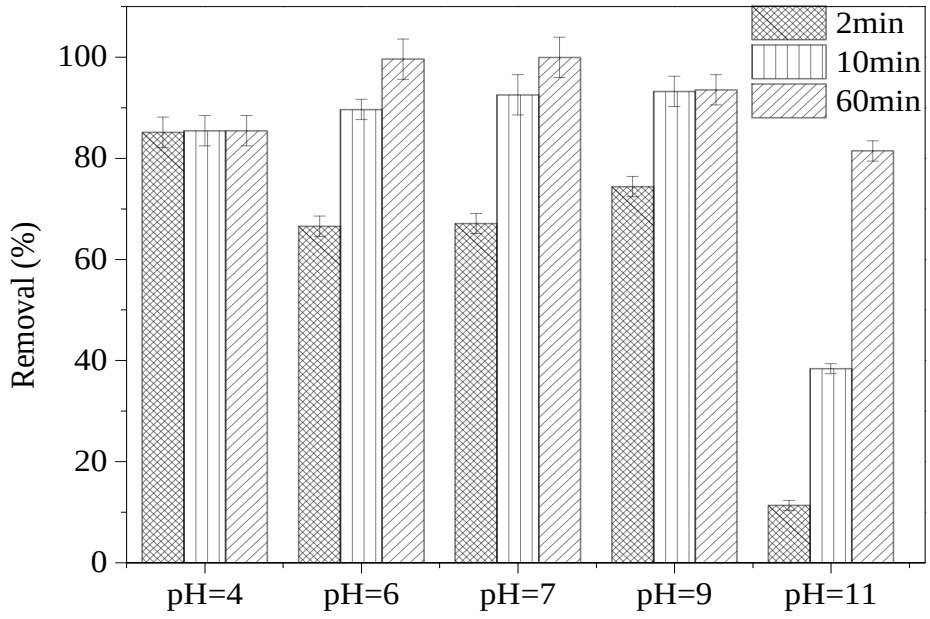
527 Fig. 1. Effect of reaction time and ferrate (VI) dosage on AAP degradation



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529 Fig. 2. Effect of different pH values on AAP degradation

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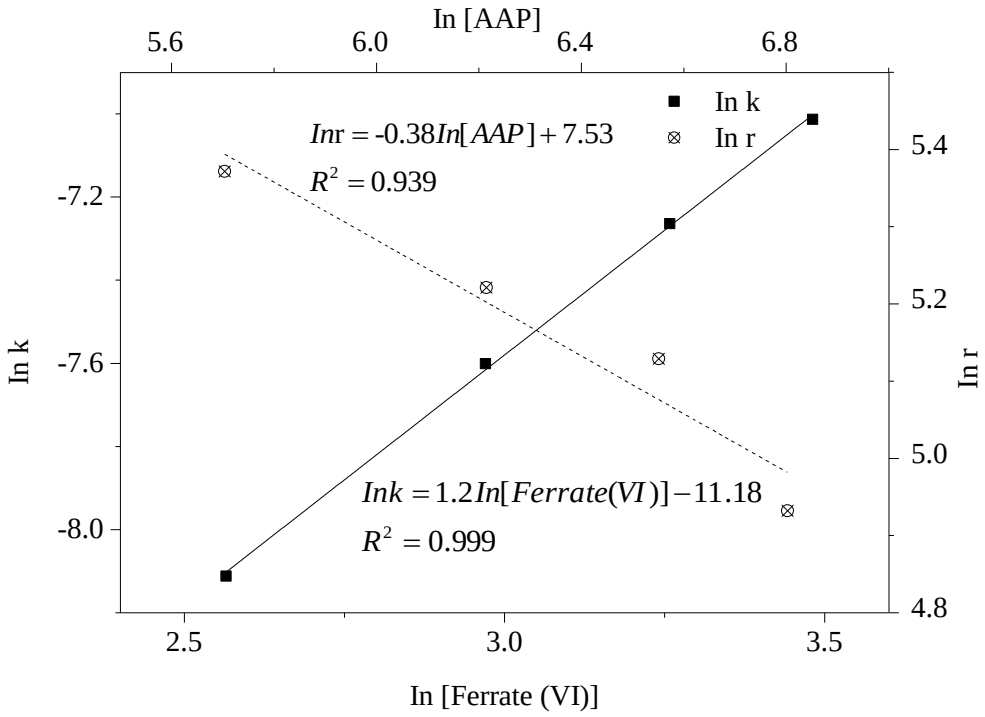

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532 Fig. 3. Kinetics analysis of AAP degradation by ferrate (VI)

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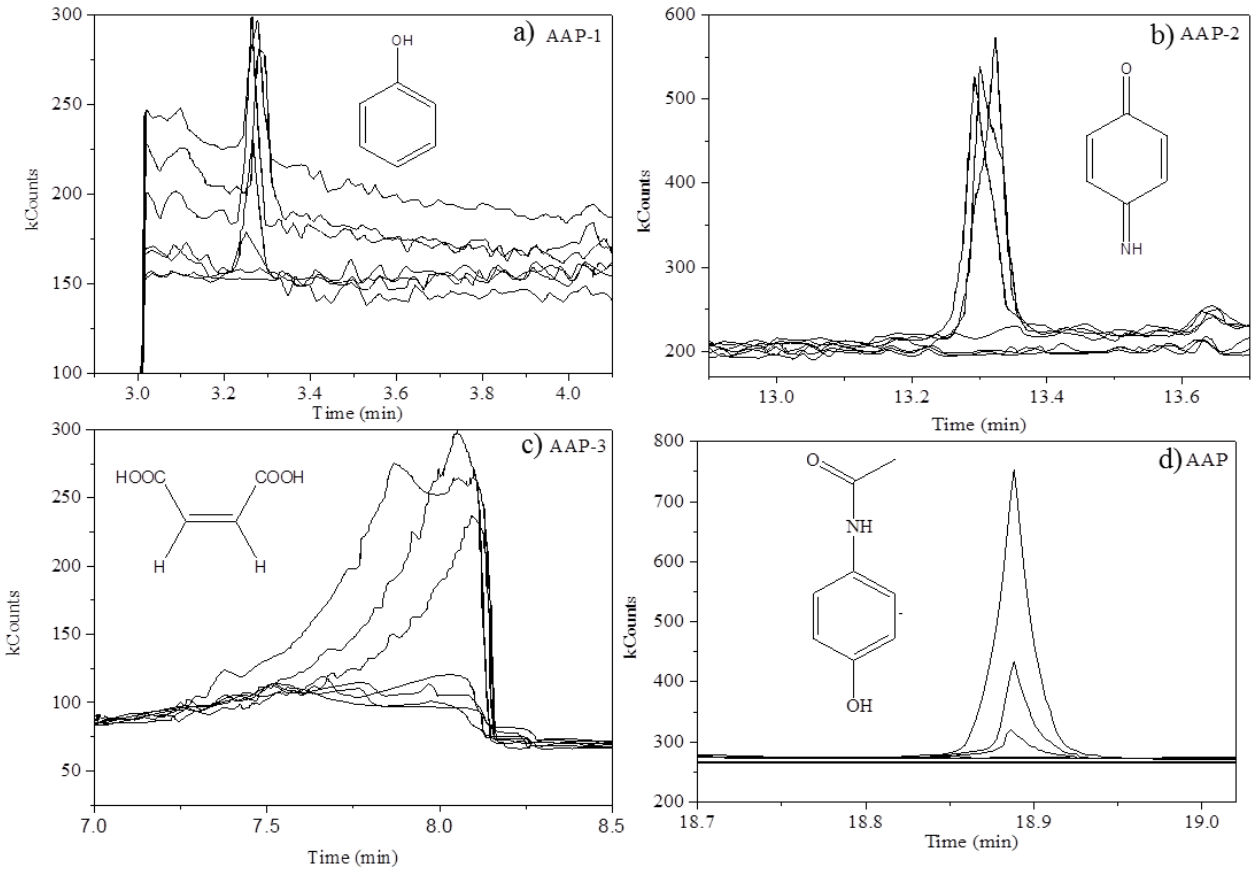

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535 Fig. 4. Detection of oxidation products (a – c) and original compound, AAP (d)

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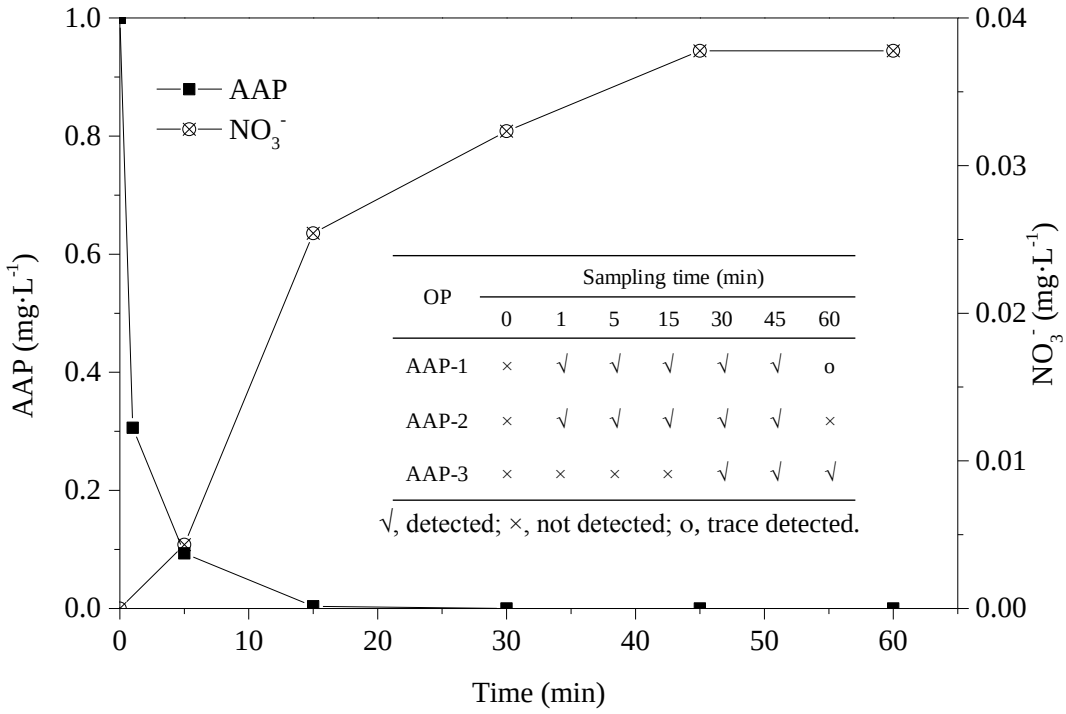

OP	Sampling time (min)						
	0	1	5	15	30	45	60
AAP-1	×	√	√	√	√	√	o
AAP-2	×	√	√	√	√	√	×
AAP-3	×	×	×	×	√	√	√

√, detected; ×, not detected; o, trace detected.

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538 Fig. 5. Evolution of OPs and nitrate with decreasing of AAP concentration

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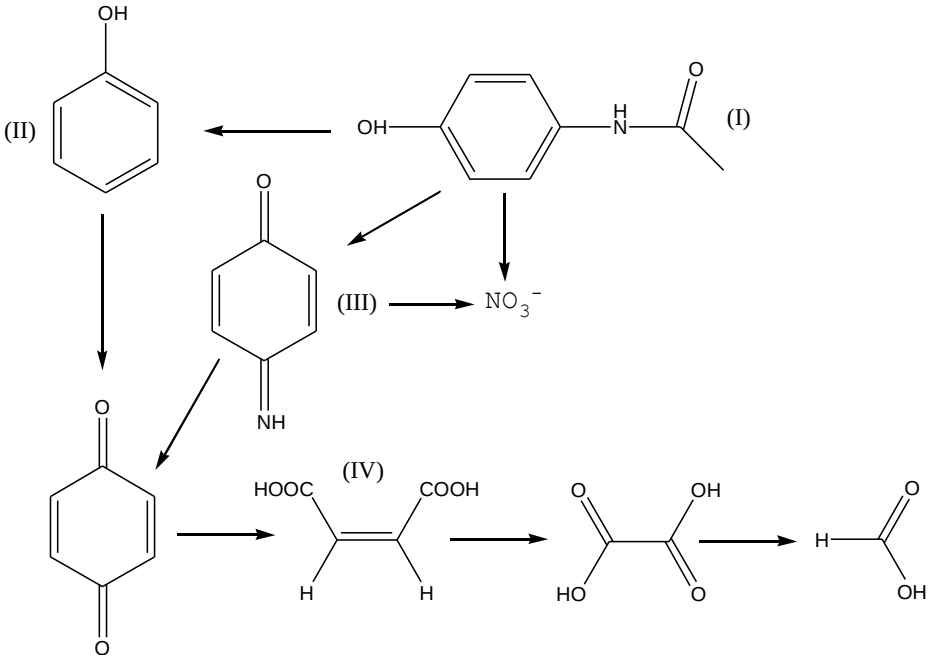
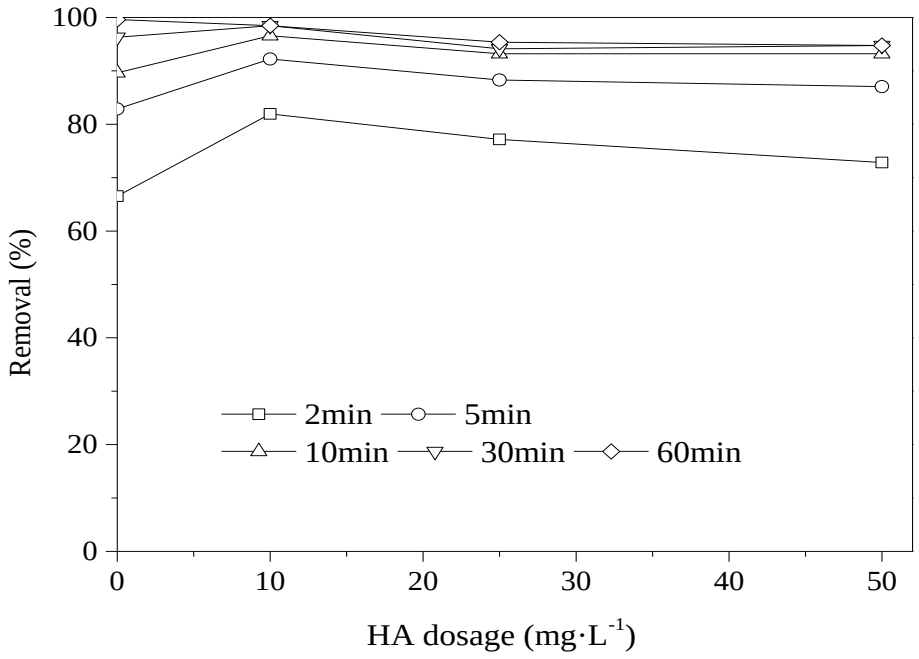


Fig. 6. Possible pathways of AAP degradation by ferrate (VI)



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543 Fig. 7. Effect of different HA dosage on AAP degradation

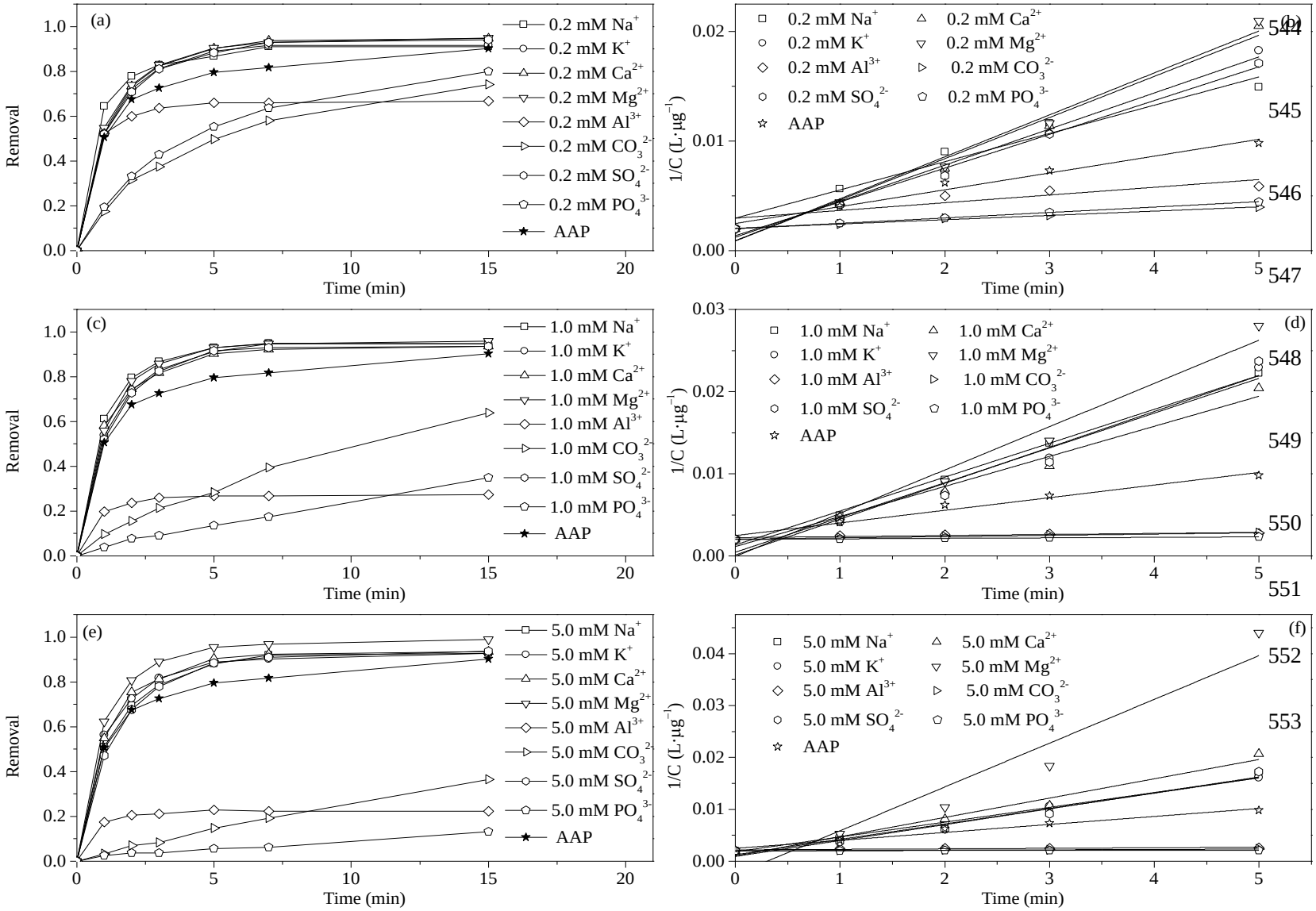

Fig. 8. Effect of different ions on AAP degradation

554 Table 1

555 Kinetic parameters of AAP degradation by ferrate (VI)

$D_{Ferate\ (VI)}$ ($mg \cdot L^{-1}$)	C_{IAAP} ($\mu g \cdot L^{-1}$)	Fitting equation	$K_{obs}(min^{-1})$	R^2	R_{IR} ($\mu g \cdot L^{-1} \cdot min^{-1}$)
13	1000	1/C=0.0003X+0.0012	0.0003	0.9093	208.3
19.5	1000	1/C=0.0005X+0.0012	0.0005	0.9946	347.2
26	1000	1/C=0.0007X+0.0013	0.0007	0.9943	414.2
32.5	1000	1/C=0.0009X+0.0012	0.0009	0.9961	625.0
32.5	900	ln C=-0.2647X+6.2611	0.2647	0.9088	138.6
32.5	700	ln C=-0.3920X+6.0656	0.3920	0.9596	168.9
32.5	500	ln C=-0.5504X+5.8182	0.5504	0.9694	185.1
32.5	300	ln C=-0.8308X+5.5569	0.8308	0.9665	215.2

556 $D_{Ferate\ (VI)}$:Ferate (VI) dosage

557 C_{IAAP}:Initial concentration of AAP

558 K_{obs}:The pseudo reaction rate constant

559 R_{IR}:Initial reaction rate

560 Table 2

561 Kinetic parameters of the AAP degradation in the presence of 8 dissolved ions

Parameter	D_{ions} (mM)	Na^+	K^+	Ca^{2+}	Mg^{2+}	Al^{3+}	CO_3^{2-}	SO_4^{2-}	PO_4^{3-}
K_{obs} (min^{-1})	0.2	0.0026	0.0033	0.0038	0.0038	0.0007	0.0004	0.0031	0.0005
R^2		0.9661	0.9905	0.9837	0.9842	0.7765	0.9944	0.9925	0.9999
K_{obs} (min^{-1})	1	0.0041	0.0042	0.0037	0.0053	0.0001	0.0002	0.0044	6.1×10^{-5}
R^2		0.9963	0.9729	0.9829	0.9700	0.6713	0.9893	0.9583	0.9789
K_{obs} (min^{-1})	5	0.0030	0.0029	0.0037	0.0084	0.0001	6.8×10^{-5}	0.0031	2.2×10^{-5}
R^2		0.9852	0.9989	0.9787	0.9340	0.6352	0.9887	0.9728	0.9012

562 D_{ion}:The ions dose

563 K_{obs}:The pseudo reaction rate constant

564

Table 3

Effect of aluminum ions on ferrate (VI) concentration

$V_{aluminum}$ (μL)	0	10	100	200	300	400	500
$C_{Ferrate\ (VI)}$ (mM)	13.2	12.8	11.5	8.9	6.6	4.3	2.8

$V_{aluminum}$:The volume of aluminum ions
$C_{Ferrate\ (VI)}$:The concentration of ferrate (VI)